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**A STUDY OF SURFACE TENSION  
DRIVEN SEGREGATION IN MONOTECTIC  
ALLOY SYSTEMS**

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**FINAL REPORT ON THE STUDY OF SURFACE TENSION DRIVEN  
SEGREGATION IN MONOTECTIC ALLOY SYSTEMS**

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**INTRODUCTION**

Considerable interest has been expressed recently in materials exhibiting liquid miscibility gaps. This interest results from predictions that these materials may exhibit superconducting properties, serve as catalysts, or exhibit high coercive magnetic field strengths [1]. Monotectic alloy systems are examples of metal-metal systems that exhibit liquid immiscibility. Specifically, alloys of hypermonotectic composition cool through a region of two liquid immiscibility during solidification, as shown in Figure 1. Due to gravitational effects and density differences between the two liquid phases,  $L_1$  and  $L_2$ , macroscopic separation of the phases usually occurs as a result of settling. This renders the material useless for the aforementioned applications.

For successful characteristics to be obtained, it is desirable to produce a fine, uniform dispersion of one phase in the other. This increases the amount of surface area per unit volume, possibly resulting in enhanced properties. [2]. Most research concerning the phase separation in hypermonotectic alloy systems has been associated solely with eliminating gravitational effects using microgravity processing. However, results have shown that the effects of non-gravitational, surface tension driven flows have been significant enough to cause macroscopic phase separation in

several cases where alloys were processed under low gravity conditions [3,4]. These surface tension effects must be controlled in order to produce useful materials.

Early research in liquid miscibility gap systems revealed that some phase separation effects were a result of wetting tendencies between the alloy and the crucible material, and therefore due to surface energies of the respective phases [5]. In solidification under microgravity conditions, phase separation may occur due to surface tension induced flows. If the minority phase, which is the  $L_2$  phase in most desirable alloys, preferentially wets the crucible wall, the result will be an increase in the tendency for separation to occur. This type of surface tension induced separation can be lessened or even avoided if the alloy system and crucible material combination is selected so that the majority phase,  $L_1$  in this study, preferentially wets the crucible material. Potard's work [5] with the aluminum-indium system and silicon carbide crucibles bore out the importance of compatibility between the crucible and alloy. Dispersed structures were obtained when this alloy system was solidified under microgravity conditions using silicon carbide crucibles. However, researchers using the same alloy system and an aluminum oxide crucible encountered massive separation during solidification [3].

Therefore, the objective of this study was to evaluate compatibility for various alloy systems when processed in combination with several different crucible materials utilizing normal solidification. Since surface energy data for this type of system is difficult to obtain and is of

rather limited accuracy, an experimental approach was designed to produce a qualitative evaluation of alloy system and crucible material compatibility. Compatibility was based on the evaluation of the wetting tendency of the two immiscible phases with the crucible material in a one-g solidified sample.

#### **PROCEDURE**

Compatibility evaluations were carried out using a small candidate alloy sample of a composition that produced fifty volume percent of each liquid phase at the monotectic temperature. This alloy was placed into a small diameter closed end tube of the selected crucible material. The alloy-crucible combination was placed in a vertically oriented quartz tube in which an argon atmosphere was maintained during melting. The sample was inductively heated to a temperature above the consolute temperature for the alloy and allowed to homogenize. Power to the induction coil was shut off and the sample allowed to solidify normally. The alloy-crucible combination was then longitudinally sectioned, mounted and polished. Microscopic examination of the contact angle of the interface between the immiscible phases and the crucible wall was utilized to determine which of the phases preferentially wet the crucible material and hence, to evaluate alloy-crucible combination compatibility.

## RESULTS

Three types of wetting phenomena were seen during the compatibility evaluation. Two of the types of results obtained were predicted before experimentation and are shown in Figure 2.

Type I indicates an alloy-crucible combination with unfavorable wetting characteristics. The  $L_2$  phase preferentially wets the crucible material. Since  $L_2$  is usually the minority phase in desirable alloys, this alloy system-crucible material combination is more difficult to process than others. The surface tension effects would have to be overcome during processing in order to produce useful structures. This type of combination is considered "incompatible" since processing is difficult.

Type II behavior indicates an alloy-crucible combination with favorable wetting characteristics. The  $L_1$  phase preferentially wets the crucible material. Hence, processing can more easily produce the desired structures. This type of combination is considered "compatible", since surface tension effects should aid in processing the alloy to a useful form.

Type III indicates any type of combination that leads to major reactions between the alloy and crucible material, gas entrapment, or separation of the metal from the crucible wall. Additional compatibility evaluations would have to be carried out on combinations in this category.

Five alloy systems were chosen for evaluation. These included aluminum-bismuth, aluminum-indium, aluminum-lead, cadmium-gallium and copper-lead. The systems were combined with crucibles of alumina, boron nitride, mullite, quartz, silicon carbide and zirconia. In the following sections, each alloy system will be reviewed with all of the crucible materials investigated.

### Aluminum-Bismuth

The aluminum-bismuth system evaluation revealed that the  $L_2$  phase preferentially wet the crucible material (Type I) for alumina and zirconia. Unexpected or Type III wetting characteristics were obtained for boron nitride, mullite, quartz and silicon carbide crucible materials. Photomicrographs of each combination are shown in Figures 3-8.

The combination of this alloy with the alumina and zirconia crucible materials (Figures 3 and 8, respectively) revealed a thin film of Bi-rich  $L_2$  phase intruding between the Al-rich  $L_1$  phase and the crucible material. This situation is undesirable for the production of a dispersed structure. The combination of the Al-Bi alloy with the boron nitride crucible material (Figure 4) revealed what seems to be a Type I interface with finite wetting but with separation of the alloy melt from the crucible material. A possible explanation of this phenomena was incomplete processing of the crucible material leading to vapor escaping from the crucible material during melting of the alloy, making this a Type III combination. In future work, the boron nitride crucible

material should be first heated to drive off vapor within the crucible walls before processing.

The mullite, quartz, and silicon carbide combinations (Figures 5, 6, and 7 respectively) were labeled as Type III wetting characteristics, indicating that reactions took place with the crucible material while processing the alloy. For mullite and quartz, a thick film of Bi-rich  $L_2$  wet the crucible material and encapsulated the Al-rich  $L_1$ . In addition, an area of reacted material was visible along the metal-crucible interface indicating a Type III combination. The silicon carbide crucible in combination with the Al-Bi alloy also had a reacted area at the crucible-metal interface. However, a finite wetting angle was present on one side, with the Bi-rich  $L_2$  phase wetting the crucible.

No crucible alloy combinations in this alloy system were recognized as completely compatible, as defined previously. However, the Al-Bi alloy in combination with the silicon carbide crucible is a candidate for further experimentation since a finite wetting angle was found.

#### Aluminum - Indium

The Al-In system evaluation revealed non-compatible Type I wetting characteristics for the alumina, mullite, quartz, and zirconia crucibles although some unexpected wetting characteristics were observed in these combinations. The boron nitride combination with the Al-In system indicated a Type III condition with finite wetting. The silicon carbide

crucible revealed the most interesting results, producing a compatible, Type II combination, in which the  $L_1$  preferentially wet the crucible material.

Photomicrographs of the combinations are shown in Figures 9-14. The silicon carbide crucible (Figure 13) displayed an almost flat interface between the two immiscible phases, indicating that the Al-rich  $L_1$  phase preferentially wet the crucible wall. Hence, this alloy-crucible combination would be considered desirable for microgravity experimentation.

The alumina, mullite, and quartz crucibles, when combined with this alloy, indicated a tendency for a Type I reaction but with a finite wetting angle. Hence these combinations (Figures 9, 11 and 12) may be desirable for processing. Usually, the  $L_2$  phase intrudes between the  $L_1$  phase and the crucible material in Type I combinations, sometimes totally encapsulating the  $L_1$  phase. Since a finite angle was present in these combinations,  $L_2$  does not tend to wet the crucible material and form a film at the crucible wall. The boron nitride crucible-alloy combination had Type III behavior with separation of the metal from the crucible material. However, a finite wetting angle was present for this combination. This intermediate case between a Type II reaction and a Type I reaction may influence the ability to produce a desirable structure after processing.

#### Aluminum-Lead

The Al-Pb system revealed several interesting results as

shown in Figures 15-20. The melts of this alloy system with alumina, boron nitride, quartz, and mullite indicated some reactive, or Type III combinations. A tendency for the lead-rich film to wet the crucible walls was noted in these combinations. When this alloy was first melted in a zirconia crucible, a Type I reaction was exhibited with a tendency for the Pb-rich  $L_2$  phase to wet the crucible wall with a thin lead film. The film encapsulated the Al-rich  $L_1$  phase. However, in two follow-up melts (Figure 20) a Type II combination was found on one side of the interface between the immiscible phases and crucible material. Small droplets of the Al-rich phase lined the  $L_2$  phase along the crucible interface.

Another interesting result came when this alloy was combined with the silicon carbide crucible (Figure 19). Although a Type I reaction was prevalent, the Al-rich  $L_1$  phase partially reacted with the crucible material. In one case there was a tendency to produce a flat interface. In several repeat melts, the interface was flat on one side of the crucible but exhibited a Type II contact on the other side. Therefore, the combination of this alloy system with zirconia and silicon carbide indicated intermediate compatibility.

#### Cadmium-Gallium

The Cd-Ga alloy system revealed a Type I or incompatible combination for all crucible materials evaluated (Figures 21-24). The Cd-rich  $L_2$  phase wet the crucible materials and intruded between the crucible wall and the Ga-rich  $L_1$  phase.

Hence, processing with this system would be difficult for all crucible materials evaluated.

### Copper-Lead

The Cu-Pb alloy system appeared to reveal a Type I combination for all crucible materials evaluated (Figures 25-27). However, several problems occurred during processing of this system leading to incomplete results in some cases.

A tendency for incomplete melting or non-homogeneity during melting interfered with the analysis of this alloy system with the alumina, silicon carbide, zirconia, and quartz crucible materials. Quartz, alumina, and zirconia indicated a tendency for a Type I combination. However, the evaluation was inconclusive since incomplete melting occurred. The Cu-Pb alloy-silicon carbide crucible combination also resulted in incomplete melting, making a compatibility evaluation impossible. The copper-lead alloy, when processed with a mullite crucible, revealed a Type I compatibility combination, with no melting difficulties visible. Overall, the Cu-Pb system showed a tendency for Type I compatibility with all crucible materials evaluated and a tendency for difficulty with melting. Hence, processing of the Cu-Pb system would be difficult.

### **DISCUSSION OF RESULTS**

Table I shows a summary of findings for all of the alloy system-crucible material combinations tested. An asterisk

indicates a combination that was not evaluated. An alloy system with a Type I compatibility combination will have varying degrees of wetting which indicate difficulty in processing. For example, a Type I combination with a finite wetting angle could be directionally solidified or processed under microgravity conditions easier than a Type I combination that exhibits total encapsulation of the  $L_1$  phase by the  $L_2$  phase. Due to the importance of this factor, Table I also indicates whether a finite angle was found.

Several combinations indicated a possibility for processing by having Type I compatibility with finite wetting. These combinations include aluminum-indium in combination with alumina. This alloy system/crucible combination has been used in microgravity directional solidification studies with varying degrees of success in processing. Other combinations showing this tendency include: Al-Bi/silicon carbide; Al-In/mullite; Al-In/quartz; Al-In/zirconia; Al-Pb/silicon carbide; Al-Pb/zirconia and Al-Pb/alumina. The above mentioned combinations have varying types or degrees of wetting, which could affect their ability to be successfully processed. Repetitive analysis would clarify these findings but is beyond the constraints of the present investigation.

From Table I, it is evident that only one of the alloy system-crucible material combinations was found to have Type II compatibility. This combination was the aluminum-indium alloy system combined with a silicon carbide crucible. This result reinforces earlier findings in Potard's work with this alloy system. This combination seems ideal for use in

microgravity solidification processing studies in immiscible systems.

## CONCLUSIONS

Several conclusions can be drawn from this investigation:

1. Crucible-alloy compatibility determination can be made using qualitative evaluation of alloy-crucible wetting tendencies under normal one-g solidification conditions.
2. Several combinations revealed Type I finite wetting, indicating a possibility for successful processing under microgravity.
3. A leading candidate for use in solidification processing of immiscible alloys in microgravity would be the Al-In alloy system with silicon carbide crucibles. This combination revealed a Type II compatibility.

## FUTURE WORK

Any future experimentation should first proceed with extensive, repetitive evaluations of the system-crucible combinations covered in this study in order to clarify any discrepancies. In addition, it would be interesting to carry out solidification studies in a particular alloy system with

compatible crucible materials and non-compatible crucible materials in order to determine differences in solidified microstructures.

#### **ACKNOWLEDGEMENTS**

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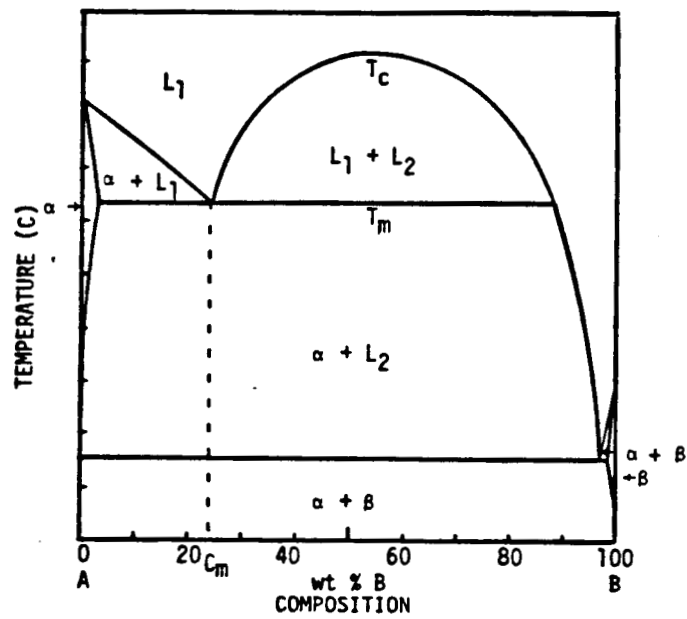
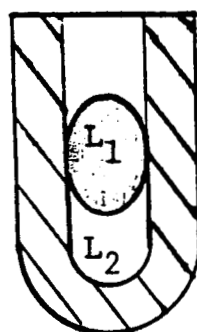
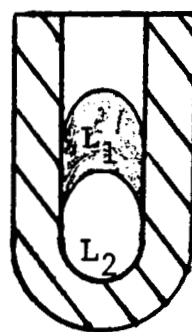


Figure 1. Binary monotectic phase diagram.



Type I



Type II

Figure 2. Two types of observed wetting. (a) Type I - non-compatible combination. (b) Type II - compatible combination.

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Figure 3. Al-Bi alloy system in combination with an alumina crucible material. Magnification 7X.

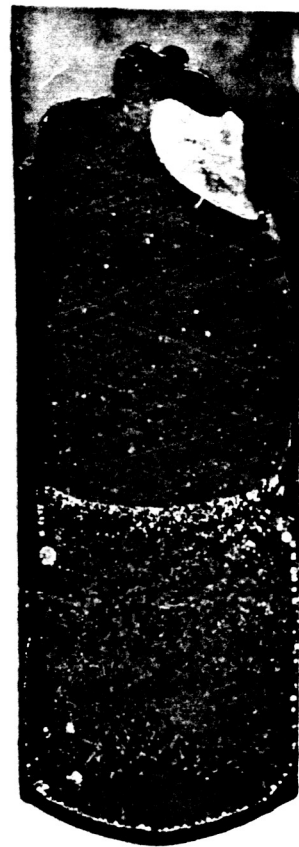


Figure 4. Al-Bi alloy system in combination with a boron nitride crucible material. Magnification 7X.

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Figure 5. Al-Bi alloy system in combination with a mullite crucible material. Magnification 7X.



Figure 6. Al-Bi alloy system in combination with a quartz crucible material. Magnification 7X.

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Figure 7. Al-Bi alloy system  
in combination with a silicon  
carbide crucible material.  
Magnification 7X.



Figure 8. Al-Bi alloy system  
in combination with a zirconia  
crucible material. Magnifica-  
tion 7X.

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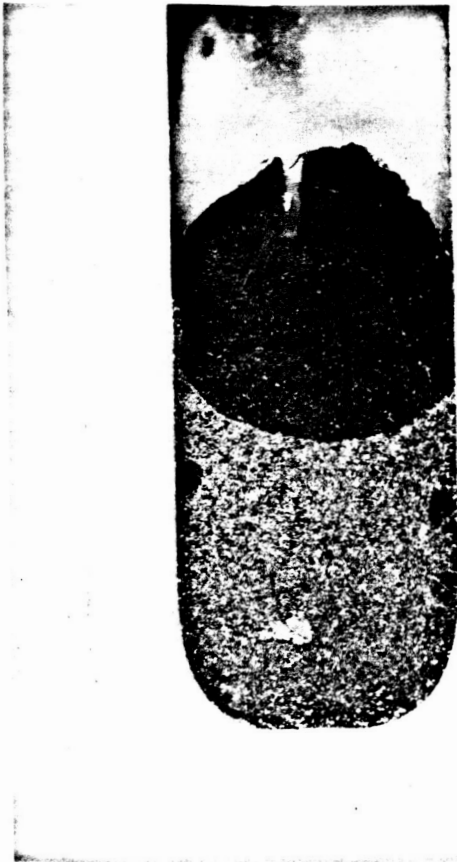


Figure 9. Al-In alloy system in combination with an alumina crucible material. Magnification 7X.

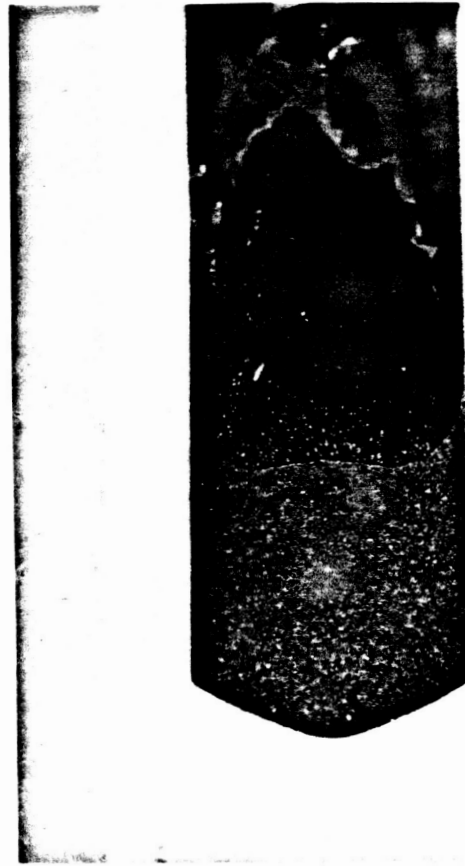


Figure 10. Al-In alloy system in combination with a boron nitride crucible material. Magnification 7X.

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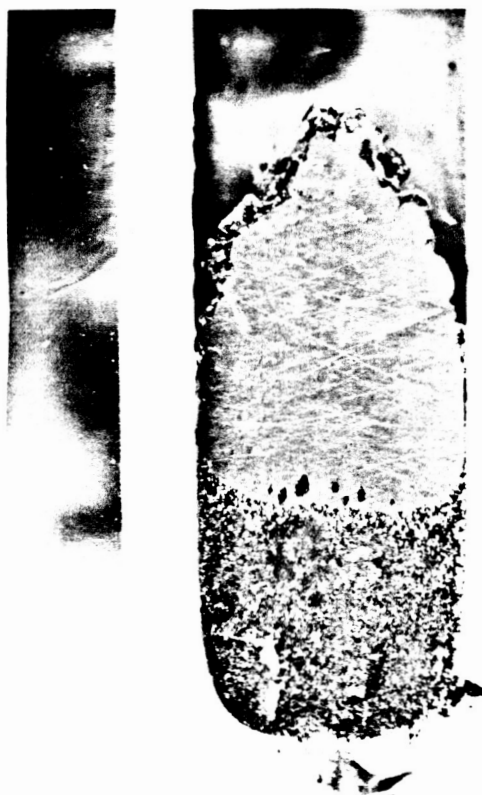


Figure 11. Al-In alloy system in combination with a mullite crucible material. Magnification 7X.



Figure 12. Al-In alloy system in combination with a quartz crucible material. Magnification 7X.

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Figure 13. Al-In alloy system in combination with a silicon carbide crucible material. Magnification 7X.



Figure 14. Al-In alloy system in combination with a zirconia crucible material. Magnification 7X.

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Figure 15. Al-Pb alloy system in combination with an alumina crucible material. Magnification 7X.



Figure 16. Al-Pb alloy system in combination with a boron nitride crucible material. Magnification 7X.

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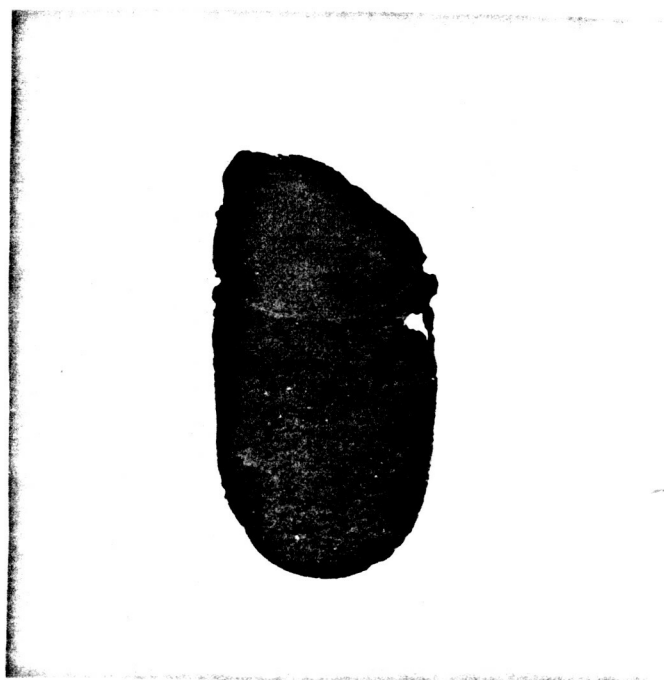


Figure 17. Al-Pb alloy system in combination with a mullite crucible material. Magnification 7X.



Figure 18. Al-Pb alloy system in combination with a quartz crucible material. Magnification 7X.

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Figure 19. Al-Pb alloy system in combination with a silicon carbide crucible material. Magnification 7X.



Figure 20. Al-Pb alloy system in combination with a zirconia crucible material. Magnification 7X.

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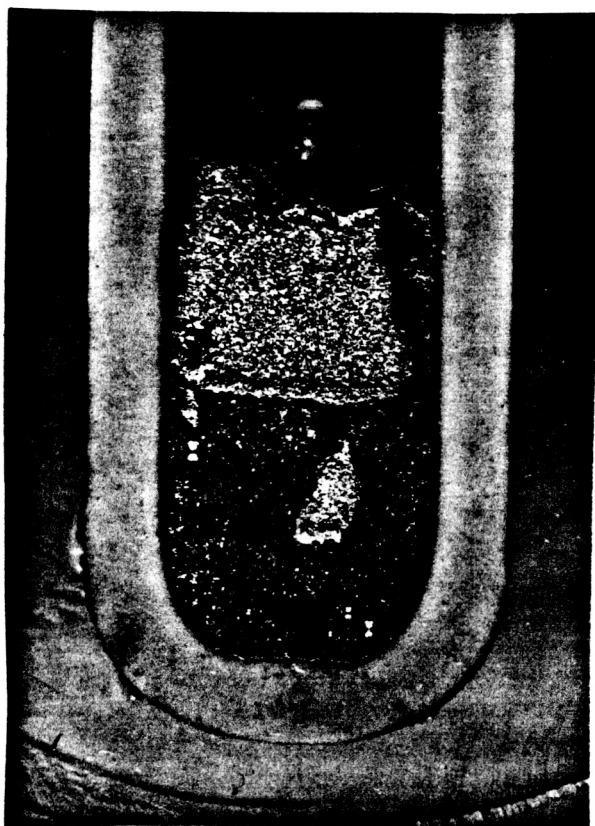


Figure 21. Cd-Ga alloy system in combination with an alumina crucible material. Magnification 7X.

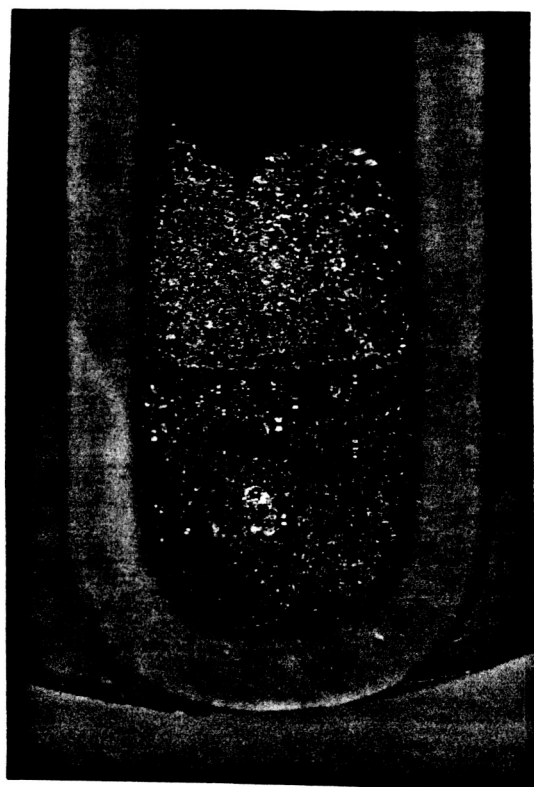


Figure 22. Cd-Ga alloy system in combination with a mullite crucible material. Magnification 7X.

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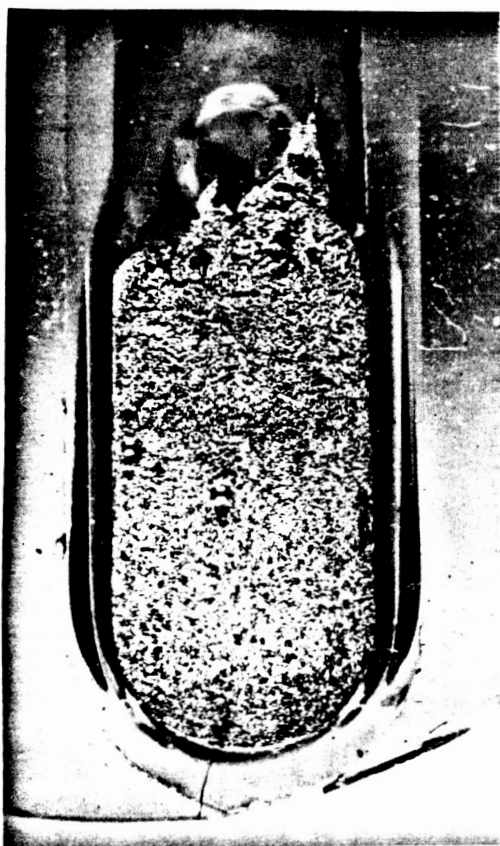


Figure 23. Cd-Ga alloy system in combination with a quartz crucible material. Magnification 7X.

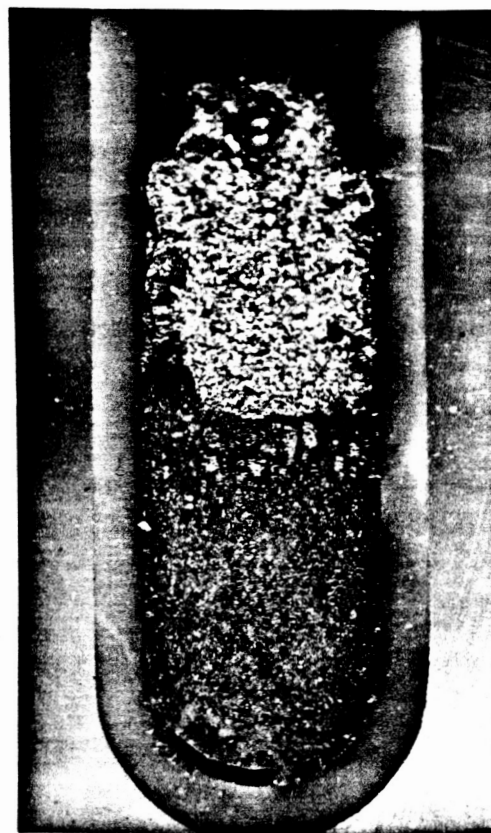


Figure 24. Cd-Ga alloy system in combination with a zirconia crucible material. Magnification 7X.

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Figure 25. Cu-Pb alloy system in combination with a mullite crucible material. Magnification 7X.



Figure 26. Cu-Pb alloy system in combination with a quartz crucible material. Magnification 7X.

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Figure 27. Cu-Pb alloy system  
in combination with a zirconia  
crucible material. Magnifica-  
tion 7X.

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Table 1. Compatibility chart of alloy system versus crucible material. Type I - non-compatible combination. Type II - compatible combination. Type III - combination with crucible reaction or other processing difficulty. (\*) - finite wetting angle

# ALLOY SYSTEMS

C  
R  
U  
C  
I  
B  
L  
E  
M  
A  
T  
E  
R  
I  
A  
L  
S

	Al-Bi	Al-In	Al-Pb	Cd-Ga	Cu-Pb
Alumina	I	I*	III*	I	I
Boron Nitride	III	III*	III	-	I
Mullite	III	I*	III	I	I
Quartz	III	I*	III	I	I
Silicon Carbide	III*	II	I*	-	I
Zirconia	I	I*	I*	I	I

Table 1. Compatibility chart of alloy system versus crucible material.

Type I - non-compatible combination

Type II - compatible combination

Type III - combination with crucible reaction  
or other processing difficulty

(\*) - finite wetting angle